

Macrocyclic Polyfunctional Lewis Bases.

XI. Structure of Trichlorocuprates of Crown-Complexed Sodium.

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Received February 25, 1984

Abstract

The structures of trichlorocuprates of benzo-15-crown-5 complexed sodium and dibenzo-18-crown-6 complexed sodium were determined from diffractometer data by direct methods and refined by least-squares to $R(F) = 0.059$ and 0.039 respectively. Both complexes, $(C_{14}H_{20}O_5)_2Na_2Cu_2Cl_6$ and $(C_{20}H_{24}O_6)_2Na_2Cu_2Cl_6$, are centrosymmetric and consist of very similar $Cu_2Cl_6^{2-}$ units lying across the centre of symmetry. Two Na^+ cations, surrounded individually by crown ether ligands, are located on opposite sides of the anion. The dimeric structure of the anion is very characteristic for chlorocuprates of very bulky cations and resembles the anions present in tetraphenylphosphonium and tetraphenylarsonium chlorocuprates. This gives a further support to the 'super heavy' alkali metal cations concept.

Introduction

The stability of numerous complex anions is strongly influenced by the size and charge [1] of the counter-ion. Illustrative examples are sodium complex halides such as chloromanganates, chlorocobaltates, chlorocuprates and chlorotellurates, all significantly less stable than complex halides of heavier alkali metals [2, 3]. Chlorocuprates [4], of which the potassium rubidium and cesium trichlorocuprates are known, are the most thoroughly studied complexes. Numerous ammonium and phosphonium chlorocuprates are also known. Sodium trichlorocuprate has not been obtained, probably due to the strong electrostatic field created by sodium ions which prevents the formation of the respective chlorocuprate [3]. In connection with

this the formation of lithium trichlorocuprate seems surprising. However the crystal structure of this compound reveals the existence of a relatively large hydrated lithium cation $(Li \cdot H_2O)^+$ [5].

Recently we described the synthesis of trichlorocuprates of crown complexed sodium in which the cation size is significantly increased [6]; moreover, the interaction of the cation with the lone electron pairs of crown ether oxygens causes dispersion of its charge enabling an increase in chlorocuprate stabilities. A similar stabilization effect of carbonylate complex anions by the 18-crown-6 complexed sodium cation has also been described [7, 8].

The cation size strongly influences the structure of chlorocuprate anion in trichlorocuprates. For very bulky tetraphenylphosphonium [9] and tetraphenylarsonium [10] cations the trichlorocuprate anions are dimeric, with strictly tetracoordinated copper. For smaller cations the anionic part becomes polymeric, and the copper coordination changes to five for medium and to six for small cations as in $KCuCl_3$ and NH_4CuCl_3 [cf. 4].

The aim of this work was to determine the effect of crown complexed sodium cations on the structure of the trichlorocuprate anions.

Experimental

Suitable crystals of trichlorocuprate of benzo-15-crown-5 complexed sodium 1 and of dibenzo-18-crown-6 complexed sodium 2 (Fig. 1) were prepared as described previously [6].

Crystallographic Data

Trichlorocuprate of benzo-15-crown-5 complexed sodium 1

Photographs taken on a Weissenberg camera showed that the crystals belonged to the mono-

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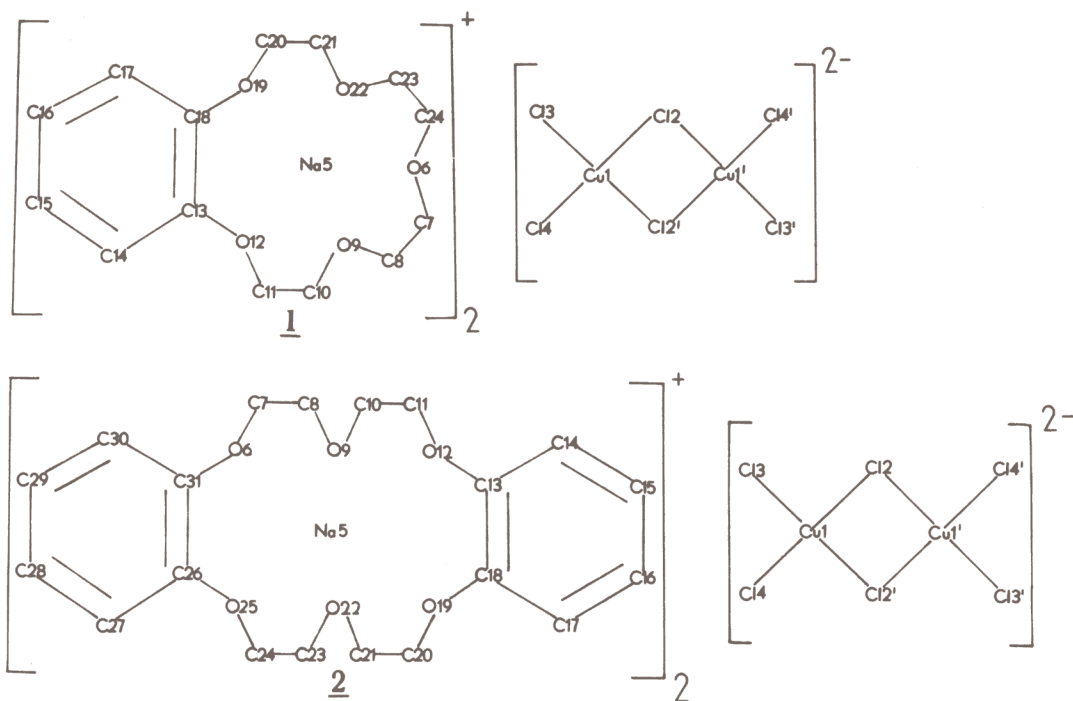


Fig. 1. The numbering schemes and formulas of complex 1 and 2.

clinic system and gave preliminary cell dimensions. Systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ determined uniquely the centrosymmetric space group $P2_1/c$. A crystal of approximate dimensions $1.1 \times 0.45 \times 0.35$ mm was mounted on a Stoe automated four-circle diffractometer with the a -axis parallel to the ϕ -axis. Accurate cell dimensions were refined by a least-squares procedure based on 2θ values for 20 high angle reflections measured on the diffractometer. Crystal data: $a = 9.805(3)$, $b = 9.449(3)$, $c = 21.382(7)$ Å, $\beta = 104.84(5)^\circ$, $V = 1915$ Å³, $D_x = 1.600$ g cm⁻³ for $Z = 2$ units, $(C_{14}H_{20}O_5)_2 \cdot Na_2Cu_2Cl_6$, MW = 922.42, $F(000) = 940$, $\mu = 58.9$ cm⁻¹. The intensity data were collected to a limit of $2\theta = 128^\circ$ with Cu-K α radiation ($\lambda = 1.54179$ Å) using the $\theta:2\theta$ scan technique. Of the total number of 3360 independent reflections 2454 with $I > 2\sigma(I)$ were classified as observed. Two standards measured every 40 reflections showed no significant deterioration in intensity during data collection (less than 2%). The intensities were corrected for Lorentz and polarisation effects. No absorption correction was applied.

Trichlorocuprate of dibenzo-18-crown-6 complexed sodium 2

A set of Weissenberg photographs determined uniquely the $P2_1/n$ space group from the following systematic absences; $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$, and allowed us to measure preliminary cell dimensions. The crystal selected for data collection had dimensions of $0.3 \times 0.4 \times 0.75$ mm and was mounted on a Stoe diffractometer with its

c -axis nearly parallel to the ϕ -axis of the goniometer. Cell dimensions were accurately refined by a least-squares fit to 25 2θ values measured on the diffractometer. Crystal data: $a = 12.754(5)$, $b = 12.006(5)$, $c = 14.996(6)$ Å, $\beta = 92.80(5)^\circ$, $V = 2293$ Å³, $D_x = 1.603$ g cm⁻³ for $Z = 2$ molecules of the formula $(C_{20}H_{24}O_6)_2Na_2Cu_2Cl_6$, MW = 1106.61, $F(000) = 1132$, $\mu = 50.6$ cm⁻¹. 3764 reflections were collected to a limit of $2\theta = 128^\circ$, and 3592 were considered as observed. Intensities of two standard reflections varied less than 4% during data collection. The intensities were corrected for Lorentz and polarisation effects. No absorption correction was applied.

Solution and Refinement of the Structures

Both structures were solved by the MULTAN program [11], the 600 highest E values being used in both cases. The E -map calculated for complex 1 clearly showed the $Cu_2Cl_6^{2-}$ group placed around the centre of symmetry, the sodium position, and a fragment of the crown ring. By two subsequent iterations of isotropic refinement and difference Fourier synthesis all the remaining non-hydrogen atoms were found and the R factor ($= \sum \|F_o| - |F_c| \| / \sum |F_o|$) dropped from 33 to 15.6%. A few more cycles of full-matrix anisotropic refinement reduced R to 7.5%. At this stage the ΔF synthesis revealed all hydrogen atoms, which were then included in the refinement with isotropic temperature factors. The final R value was 5.9%. Apart from the few peaks of ca. 0.6 e Å⁻³ around the $Cu_2Cl_6^{2-}$ group the highest

TABLE I. Atomic Positional Parameters ($\times 10^4$) with E.s.d.'s in Parentheses for Non-hydrogen Atoms for Complex 1.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
Cu1	9236(1)	5498(1)	569(1)	435
Cl2	9823(2)	6558(1)	-290(1)	521
Cl3	9697(2)	7260(2)	1260(1)	586
Cl4	7428(2)	4580(2)	855(1)	735
Na5	6975(3)	6962(2)	1637(1)	484
O6	7823(6)	5757(5)	2670(2)	679
C7	6896(12)	4772(12)	2847(5)	894
C8	5861(12)	4252(9)	2254(5)	798
O9	5117(5)	5455(5)	1929(2)	632
C10	4163(9)	5119(8)	1331(4)	690
C11	3484(8)	6450(8)	1018(4)	590
O12	4590(5)	7453(4)	1013(2)	516
C13	4177(7)	8784(7)	769(3)	483
C14	2873(9)	9117(9)	373(4)	624
C15	2551(10)	10458(10)	147(4)	736
C16	3553(10)	11487(9)	318(4)	697
C17	4874(10)	11204(8)	715(4)	619
C18	5194(7)	9843(6)	952(3)	458
O19	6475(5)	9436(4)	1352(2)	497
C20	7197(9)	10498(8)	1806(4)	631
C21	8444(9)	9811(8)	2242(4)	654
O22	7988(5)	8611(5)	2528(2)	616
C23	9121(10)	7847(10)	2939(4)	727
C24	8532(12)	6629(11)	3199(4)	821

$$U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha), \text{ cf. [15].}$$

density on the final difference Fourier map was 0.4 eÅ⁻³. None of the positional parameters of the non-hydrogen atoms shifted more than 0.04σ in the last cycle of refinement.

The E-map of complex 2 structure revealed all 31 non-hydrogen atoms. A few cycles of isotropic and anisotropic refinement diminished the R factor from 18.6 to 5.4% and allowed us to find all hydrogen atoms on the difference Fourier map. Hydrogen atoms were included in the refinement with isotropic temperature factors. After four more cycles of full-matrix refinement the R factor dropped to the final value of 3.6%. The highest electron density on the final difference Fourier map was 0.35 eÅ⁻³, except for two_{peaks} of 0.5 eÅ⁻³ in the vicinity of the Cu₂Cl₆²⁻ anion. The largest shift of positional parameters of the heavy atoms in the last cycle of refinement was 0.05σ.

Calculated absorption correction in both structures yielded no lower R factor and did not improve the geometry, and was finally not taken into account. Anomalous dispersion corrections Δf' and Δf'' for all the non-hydrogen atoms were used. Atomic scattering factors for C, O, Cu, Cl and Na⁺ were taken from Cromer and Mann [12] and for H from Stewart *et al.* [13]. All computations were performed on a

TABLE II. Bond Distances (Å) and Angles (°) for Complex 1.

Chlorocuprate anion			
Cu1–Cl2	2.292(2)	Cl2–Cu1–Cl2'	87.8(1)
Cu1–Cl3	2.194(2)	Cl2–Cu1–Cl3	99.1(1)
Cu1–Cl4	2.196(2)	Cl2–Cu1–Cl4	141.5(1)
Cu1–Cl2'	2.294(2)	Cl3–Cu1–Cl2'	142.2(1)
Cu1–Cu1'	3.306(1)	Cl3–Cu1–Cl4	98.9(1)
		Cl4–Cu1–Cu2'	98.3(1)
		Cu1–Cl2–Cu1'	92.2(1)
Coordination of Na ⁺ cation			
Na5–Cl3	2.992(3)		
Na5–Cl4	2.905(3)		
Na5–O6	2.434(5)		
Na5–O9	2.513(6)		
Na5–O12	2.422(5)		
Na5–O19	2.434(5)		
Na5–O22	2.465(5)		
Crown part			
O6–C7	1.418(13)	C7–O6–C24	112.5(7)
O6–C24	1.427(10)	O6–C7–C8	109.4(8)
C7–C8	1.491(13)	C7–C8–O9	107.6(7)
C8–O9	1.431(10)	C8–O9–C10	113.4(6)
O9–C10	1.414(9)	O9–C10–C11	109.3(6)
C10–C11	1.498(11)	C10–C11–O12	107.8(6)
C11–O12	1.442(9)	C11–O12–C13	116.9(5)
O12–C13	1.382(7)	O12–C13–C14	125.2(6)
C13–C14	1.377(9)	O12–C13–C18	115.3(5)
C13–C18	1.396(9)	C14–C13–C18	119.5(6)
C14–C15	1.365(13)	C13–C14–C15	121.6(8)
C15–C16	1.364(13)	C14–C15–C16	118.8(8)
C16–C17	1.381(12)	C15–C16–C17	121.6(8)
C17–C18	1.388(9)	C16–C17–C18	119.5(7)
C18–O19	1.382(7)	C13–C18–C17	119.0(6)
O19–C20	1.448(9)	C13–C18–O19	116.4(5)
C20–C21	1.484(11)	C17–C18–O19	124.6(6)
C21–O22	1.414(10)	C18–O19–C20	115.7(5)
O22–C23	1.425(10)	O19–C20–C21	107.5(6)
C23–C24	1.460(14)	C20–C21–O22	108.7(6)
		C21–O22–C23	112.9(6)
		O22–C23–C24	108.2(8)
		O6–C24–C23	108.3(6)

CDC Cyber 175 computer at the Wissenschaftliche Rechenzentrum Berlin with an X-RAY system [14] and the MULTAN program [11].

The final positional parameters are given in Tables I and V. Parameters for H-atoms and thermal parameters have been deposited as supplementary material.

Results

Description of the Structures

The bond lengths and angles for benzo-15-crown-5 and dibenzo-18-crown-6 complexes are collected in

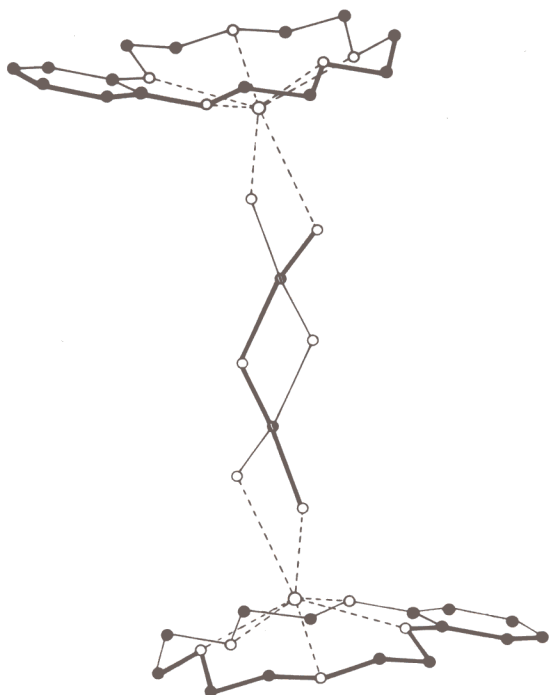


Fig. 2. Structure of complex 1.

TABLE III. Selected Torsion Angles (°) for Complex 1.

Cl2—Cu1'—Cu1—Cl3	52.7
Cl2—Cu1'—Cu1—Cl4	126.9
C24—O6—C7—C8	-161.1
C7—O6—C24—C23	162.7
O6—C7—C8—O9	58.5
C7—C8—O9—C10	-175.9
C8—O9—C10—C11	177.7
O9—C10—C11—O12	-50.9
C10—C11—O12—C13	177.1
C11—O12—C13—C18	-160.5
O12—C13—C18—O19	0.2
C13—C18—O19—C20	147.8
C18—O19—C20—C21	-173.0
O19—C20—C21—O22	55.1
C20—C21—O22—C23	-177.9
C21—O22—C23—C24	179.3
O22—C23—C24—O6	-60.9

Tables II and VI respectively (*cf.* Fig. 1). As shown in Figs. 2 and 3, both structures contain discrete dimeric $\text{Cu}_2\text{Cl}_6^{2-}$ anions lying across the centres of symmetry and on both sides accompanied by two Na^+ cations and two crown ligands.

The $\text{Cu}_2\text{Cl}_6^{2-}$ units are very similar in both structures and consist of Cu_2Cl_2 squares, built by two copper atoms and two bridging chlorines, and of two pairs of terminal chlorines at slightly shorter distances from copper, placed asymmetrically on both sides of

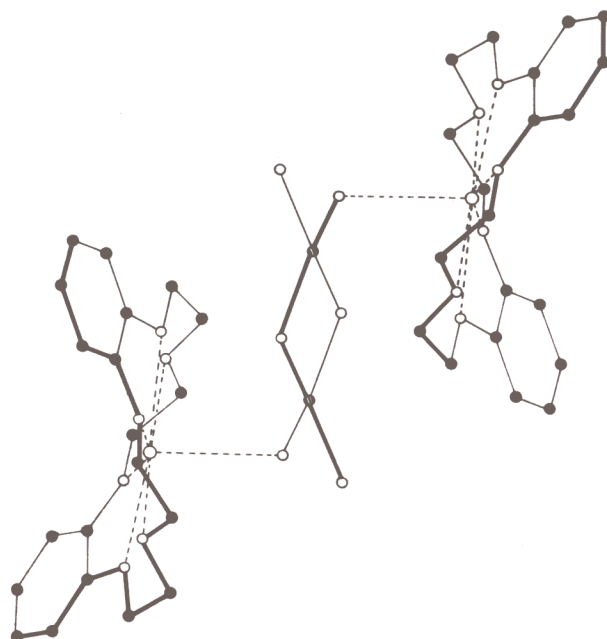


Fig. 3. Structure of complex 2.

the plane of the square so that the coordination around each copper atom is intermediate between planar and tetrahedral. The details of the conformation of $\text{Cu}_2\text{Cl}_6^{2-}$ anions in the discussed structures are summarized in Table IX, together with relevant data for two other similar known structures.

The benzo-15-crown-5 ligand exhibits some approximate symmetry, with the mirror perpendicular to the crown plane and bisecting the aromatic ring and the O6 atom. The five oxygen atoms lie within 0.36 Å in one plane (Table IV) and torsion angles on both sides of the above mentioned mirror plane correspond in pairs with opposite signs, except for those about the bonds closest to the aromatic ring (Table III). The single C—C bonds have alternate *syn*-clinal conformations and C—O bonds exhibit anti-periplanar conformation (torsion angles $180 \pm 7^\circ$), again except for the two closest to the aromatic ring, which are distorted by the planarity requirements of the ring.

The dibenzo-18-crown-6 ring system exhibits approximate *mm* symmetry. The six oxygen atoms lie in a plane, within a 0.21 Å margin. All single C—C bonds are in *syn*-clinal conformation and all C—O bonds have anti-periplanar conformation (torsion angles $180 \pm 9^\circ$) (Tables VII and VIII).

In both structures the Na^+ cation lies between the $\text{Cu}_2\text{Cl}_6^{2-}$ anion and the crown ring, and is irregularly coordinated by five (or six) oxygens and two (or one) terminal chlorines respectively. In the structure of complex 2 only one chlorine atom is coordinated by a Na^+ cation (2.834 Å), and its bond to copper is slightly longer (2.246 Å) than the Cu—Cl

TABLE IV. Least-squares Planes with Deviations of Atom Positions (in Å) for Complex 1. Atoms defining the planes are asterisked.

Aromatic ring	
C13*	−0.006
C14*	0.000
C15*	0.004
C16*	−0.002
C17*	−0.005
C18*	0.009
O12	−0.024
O19	0.008
Anion	
Cu1*	0
Cu1'*	0
Cl2*	0
Cl2'*	0
Cl3	1.316
Cl4	−1.345
Oxygen atoms	
O6*	−0.362
O9*	0.271
O12*	−0.081
O19*	−0.160
O22*	0.332
Na5	−0.960

TABLE V. Atomic Positional Parameters ($\times 10^4$) with E.s.d.s in Parentheses for Non-hydrogen Atoms for Complex 2.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^a
Cu1	8706(1)	4780(1)	9991(1)	365
Cl2	10040(1)	5038(1)	11046(1)	446
Cl3	7400(1)	5514(1)	10752(1)	432
Cl4	7805(1)	3516(1)	9224(1)	548
Na5	6985(1)	7662(1)	10035(1)	461
O6	9106(2)	7829(3)	9961(2)	447
C7	9690(3)	8198(4)	10755(3)	468
C8	9047(3)	7912(4)	11521(3)	444
O9	8080(2)	8500(2)	11418(2)	409
C10	7464(3)	8400(4)	12175(3)	454
C11	6518(3)	9110(4)	12034(3)	463
O12	5952(2)	8712(2)	11256(2)	381
C13	4970(3)	9147(3)	11077(3)	322
C14	4546(4)	10035(4)	11518(3)	419
C15	3532(4)	10389(4)	11276(3)	462
C16	2960(4)	9864(4)	10607(3)	487
C17	3386(3)	8974(4)	10156(3)	439
C18	4383(3)	8617(3)	10390(3)	327
O19	4892(2)	7738(2)	10009(2)	397
C20	4317(3)	7136(4)	9312(3)	431
C21	5029(3)	6259(4)	9005(3)	404
O22	5908(2)	6779(2)	8641(2)	380
C23	6569(3)	6026(4)	8203(3)	415
C24	7442(3)	6681(4)	7842(3)	422

TABLE V. (continued)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^a
O25	8003(2)	7195(2)	8586(2)	380
C26	8918(3)	7732(3)	8407(3)	357
C27	9251(4)	7958(4)	7559(3)	455
C28	10197(4)	8505(4)	7466(4)	554
C29	10800(4)	8819(4)	8196(4)	615
C30	10475(4)	8603(4)	9053(4)	541
C31	9525(3)	8071(3)	9154(3)	386

^a*U*_{eq} explained in Table I.

TABLE VI. Bond Distances (Å) and Angles (°) for Complex 2.

Chlorocuprate anion			
Cu1–Cl2	2.287(1)	Cl2–Cu1–Cl2'	86.4(1)
Cu1–Cl2'	2.294(1)	Cl2–Cu1–Cl3	98.0(1)
Cu1–Cl3	2.246(1)	Cl2–Cu1–Cl4	144.0(1)
Cu1–Cl4	2.194(1)	Cl3–Cu1–Cl2'	150.0(1)
Cu1–Cu1'	3.341(1)	Cl3–Cu1–Cl4	98.9(1)
		Cl4–Cu1–Cl2'	94.3(1)
		Cu1–Cl2–Cu1'	93.6(1)

Coordination of Na⁺ cation

Na5–Cl3	2.834(2)
Na5–O6	2.719(3)
Na5–O9	2.642(3)
Na5–O12	2.639(3)
Na5–O19	2.670(3)
Na5–O22	2.665(3)
Na5–O25	2.644(3)

Crown part

O6–C7	1.442(5)	C7–O6–C31	116.9(3)
O6–C31	1.379(5)	O6–C7–C8	106.6(3)
C7–C8	1.485(6)	C7–C8–O9	108.0(4)
C8–O9	1.422(5)	C8–O9–C10	112.4(3)
O9–C10	1.418(5)	O9–C10–C11	108.4(4)
C10–C11	1.485(7)	C10–C11–O12	107.5(4)
C11–O12	1.425(5)	C11–O12–C13	117.0(3)
O12–C13	1.371(5)	O12–C13–C14	125.3(4)
C13–C14	1.380(6)	O12–C13–C18	115.0(3)
C13–C18	1.397(5)	C14–C13–C18	119.8(4)
C14–C15	1.390(6)	C13–C14–C15	119.6(4)
C15–C16	1.367(7)	C14–C15–C16	120.4(4)
C16–C17	1.392(7)	C15–C16–C17	120.3(4)
C17–C18	1.371(6)	C16–C17–C18	119.7(4)
C18–O19	1.378(5)	C13–C18–C17	120.2(4)
O19–C20	1.441(5)	C13–C18–O19	114.1(3)
C20–C21	1.479(6)	C17–C18–O19	125.6(4)
C21–O22	1.415(5)	C18–O19–C20	116.8(3)
O22–C23	1.417(5)	O19–C20–C21	106.4(3)
C23–C24	1.487(6)	C20–C21–O22	108.4(3)
C24–O25	1.436(5)	C21–O22–C23	113.4(3)
O25–C26	1.371(5)	O22–C23–C24	107.8(3)
C26–C27	1.387(6)	C23–C24–O25	107.3(3)

(continued overleaf)

TABLE VI. (continued)

C26–C31	1.391(6)	C24–O25–C26	116.5(3)
C27–C28	1.385(7)	O25–C26–C27	125.1(4)
C28–C29	1.360(8)	O25–C26–C31	115.2(4)
C29–C30	1.395(8)	C27–C26–C31	119.8(4)
C30–C31	1.385(6)	C26–C27–C28	119.6(4)
		C27–C28–C29	120.8(5)
		C28–C29–C30	120.5(5)
		C29–C30–C31	119.2(5)
		O6–C31–C26	114.9(4)
		O6–C31–C30	124.9(4)
		C26–C31–C30	120.2(4)

TABLE VII. Selected Torsion Angles (°) for Complex 2.

Cl2–Cu1'–Cu1–Cl3	–43.0
Cl2–Cu1'–Cu1–Cl4	132.4
C31–O6–C7–C8	–176.1
C7–O6–C31–C26	178.0
O6–C7–C8–O9	61.5
C7–C8–O9–C10	172.2
C8–O9–C10–C11	–175.5
C10–C11–O12–C13	–170.7
O9–C10–C12–O12	–60.6
C11–O12–C13–C18	170.8
O12–C13–C18–O19	–0.3
C13–C18–O19–C20	–178.3
C18–O19–C20–C21	–179.0
O19–C20–C21–O22	62.8
C20–C21–O22–C23	171.1
C21–O22–C23–C24	–179.0
O22–C23–C24–O25	–61.1
C23–C24–O25–C26	–172.4
C24–O25–C26–C31	170.5
O25–C26–C31–O6	0.9

TABLE VIII. Least Squares Planes with Deviations of Atoms (in Å) for Complex 2.

Aromatic ring A		Aromatic ring B	
C13 ^a	–0.003	C26 ^a	–0.008
C14 ^a	0.002	C27 ^a	0.001
C15 ^a	0.001	C28 ^a	0.004
C16 ^a	–0.003	C29 ^a	–0.002
C17 ^a	0.002	C30 ^a	–0.005
C18 ^a	0.001	C31 ^a	0.010
O12	–0.015	O6	0.035
O19	–0.015	O25	–0.017
Anion		Oxygen atoms	
Cu1 ^a	0	O6 ^a	–0.017
Cu1' ^a	0	O9 ^a	–0.195
Cl2 ^a	0	O12 ^a	0.207
Cl2' ^a	0	O19 ^a	–0.010
C13	1.106	O22 ^a	–0.201
Cl4	–1.289	O25 ^a	0.217
		Na5	–0.177

^a Atoms defining the planes.

bond to the 'free' terminal chlorine (2.194 Å). In the structure of complex 1 both terminal chlorine atoms are engaged in coordination around Na⁺, with distances of 2.905 and 2.992 Å. The coordination number of the Na⁺ cation in both structures is 7.

The Na⁺ cation is enclosed to a greater degree within dibenzo-18-crown-6 ring than the benzo-15-crown-5 ring, the distances of Na⁺ from the least-squares planes of the oxygen atoms are 0.177 and 0.960 Å respectively.

Discussion

Crystal structures of both compound 1 and compound 2 (Figs. 2 and 3) consist of benzo-15-crown-5 complexed sodium cations or dibenzo-18-crown-6 complexed sodium cations, respectively, attached to the discrete hexachlorodocuprate Cu₂Cl₆^{2–} anion. The geometry of both compounds is centrosymmetric.

In general, the structures of crown-complexed sodium cations are very similar to other examples [16, 17]. The Na⁺ cation is better enclosed within dibenzo-18-crown-6 (the Na⁺–least-squares plane distance is 0.177 Å, Table VIII) than by benzo-15-crown-5 (the distance is equal to 0.960 Å, Table IV). The coordination number of the sodium cation is in both cases 7, the donor atoms being 5 or 6 crown oxygen atoms and 2 or 1 terminal chlorine atoms respectively.

The electrostatic field around the complexed sodium cation is strongly reduced, due to Na⁺ coordination to electron donating atoms and due to significant enlargement of its formal size. The formation of trichlorocuprate of crown complexed sodium is thus possible in contrast to the 'free' sodium cation, which is not able to form chlorocuprates at all [1–3, 6]. The reduction of the electrostatic field density around the complexed sodium cation, or the size of such a modified cation, can be deduced from the structural data obtained for the anionic part of both complexes.

The structure of the anionic part of trichlorocuprates depends strongly on the counter-ion properties. The existence of discrete dimeric Cu₂Cl₆^{2–} anions in the both complexes is attributable to the presence of very large counter-ions. Comparison of the structural parameters of the dimeric anions Cu₂Cl₆^{2–} in our complexes, and in tetraphenylphosphonium and tetraphenylarsonium trichlorocuprate [9, 10], reveals their great similarity (Table IX) in all respects, including the coordination number 4 of copper atoms. The structures of the anionic part of our complexes are thus comparable to the anion structure in trichlorocuprates of only very bulky tetraphenylphosphonium and tetraphenylarsonium cations, indicating a similarity in behaviour of crown-

TABLE IX. Conformation of Cu₂Cl₆⁻² Anion.

	Complex 1	Complex 2	Ph ₄ P ⁺	Ph ₄ As ⁺
Cu—Cu distance	3.341	3.306	3.355	3.382
Bridging Cu—Cl	2.287	2.292	2.292	2.305
	2.294	2.294	2.321	2.333
Terminal Cu—Cl	2.194	2.194	2.179	2.198
	2.246	2.196	2.200	2.215
Angles within the Cu ₂ Cl ₂ square				
Cl—Cu—Cl	86.4	87.8	86.7	86.3
Cu—Cl—Cu	93.6	92.2	93.3	93.7
Largest Cl—Cu—Cl angle	150.0	142.2	143.6	145.2
Distances of the terminal Cl from the plane of the square	1.106	1.316	1.294 ^a	1.25
	1.289	1.345	1.294 ^a	1.25
Torsion angle between the plane of terminal Cl ₂ Cu and Cu ₂ Cl ₂ square along the Cu—Cu line	45	53	50	66

^aCalculated from published data [9].

complexed sodium to the two last mentioned cations. Crown-complexed sodium cations behave as larger cations than the cesium ion [4]. This gives a further support to Lehn's concept [18] of 'super heavy' alkali metal cations.

Complexation of metal cations by crowns should in general affect the stability of numerous complex anions other than trichlorocuprates.

Acknowledgement

A partial financial support of this work from the MR.I-11 problem is kindly acknowledged.

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